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14. ABSTRACT

Collisional quenching of electronically excited OH $A\,^2\Sigma^+$ radicals by molecular partners has been investigated over the past 25 years, principally by evaluating the quenching cross sections for partners of aeronautical, atmospheric, and/or combustion relevance. Yet little is known about the outcome of these electronic quenching events, except that they facilitate the efficient removal of OH from the excited $A\,^2\Sigma^+$ electronic state by introducing nonradiative decay pathways. Most recently, we carried out the first experimental investigation of the nonreactive decay channel with molecular hydrogen by examining the quantum state distribution of the ground state OH $X\,^2\Pi$ products. The OH $X\,^2\Pi$ product state distribution is highly nonstatistical, with a strongly inverted rotational distribution for $v''=1$, demonstrating that a significant torque is applied to OH as purely electronic energy is converted into internal excitation of the OH $X\,^2\Pi$ products. The high degree of rotational excitation is a direct manifestation of the forces in the vicinity of the conical intersection region(s) that lead to quenching.

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AFOSR Final Report

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Quenching Dynamics of Electronically Excited Hydroxyl Radicals

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Objectives

A series of laboratory experiments has been concluded that examine the quenching dynamics of electronically excited hydroxyl radicals via collision-induced processes. The goal of these experiments was to elucidate the mechanism for nonadiabatic processes that transform electronically excited OH $A\,^2\Sigma^+$ radicals into ground state OH $X\,^2\Pi$ or reaction products. The research program encompassed studies of (1) quenching of OH $A\,^2\Sigma^+$ (v′=0) by thermospheric gases through reactive and nonreactive pathways, (2) reactive quenching of OH $A\,^2\Sigma^+$ (v′=0) by ground state hydroxyl radicals, and (3) reactive quenching of OH $A\,^2\Sigma^+$ (v′=0) by methyl radicals. The kinetic energy profile and/or quantum state distribution of the H (^{2}S), O (^3P_J), and OH $X\,^2\Pi$ products will be ascertained from spectroscopic measurements and interpreted in the context of complementary first principles theoretical calculations. The research is addressing the role of nonadiabatic interactions in fundamental chemical processes, revealing the dynamical signatures associated with curve crossings and conical intersections between two or more potential energy surfaces. This study is of direct AFOSR relevance as the *reverse* chemical reactions, O (^{3}P) + $H_2O \rightarrow$ OH $A\,^2\Sigma^+$ + OH and O (^{3}P) + $CH_4 \rightarrow$ OH $A\,^2\Sigma^+$ + CH_3, are possible sources of the OH $A \rightarrow X$ emission from the Space Shuttle's thruster plume. These laboratory measurements are needed to understand the chemical excitation pathways that lead to electronically excited OH $A\,^2\Sigma^+$ radicals in the interaction of the spacecraft's exhaust plume with the atomic oxygen atmosphere at orbital altitudes.

Accomplishments

This section summarizes our accomplishments during a terminal period of AFOSR

funding ($20,000) from 15-May-2007 to 30-Nov-2007 and the relevant portions of the prior three years of AFOSR funding, 1-Feb-2004 through 31-Dec-2006. We made significant progress on studies of the nonreactive outcome of OH $A\ ^2\Sigma^+$ collisional quenching events with H_2 and D_2.

Collisional quenching of electronically excited OH $A\ ^2\Sigma^+$ radicals by molecular partners has been extensively investigated over the past 25 years, principally by evaluating the quenching cross sections for partners of atmospheric and/or combustion relevance. Yet little is known about the outcome of these electronic quenching events, except that they facilitate the efficient removal of OH from the excited $A\ ^2\Sigma^+$ electronic state by introducing nonradiative decay pathways. For molecular hydrogen, Walch[1] and Yarkony[2] predict that the nonadiabatic pathways involve passage through conical intersection regions, which lead to ground state OH $X\ ^2\Pi$ radicals (nonreactive quenching) or reaction products. Previously, we made the first measurements of the reactive quenching process by characterizing the Doppler profiles of the H/D-atom products from collisions of electronically excited OH $A\ ^2\Sigma^+$ (v′=0) with H_2/D_2.[3]

In this grant period, we carried out the first experimental investigation of the nonreactive decay channel by examining the quantum state distribution of the ground state OH $X\ ^2\Pi$ products.[4] In this work, a UV laser prepares the OH $A\ ^2\Sigma^+$ (v′=0, N′=0) level in the collisional region of a pulsed supersonic expansion. After a short delay, a second UV laser probes the OH $X\ ^2\Pi$ (v″, J″) produced from collisional quenching by exciting various rovibrational lines of the OH A-X transition, and collecting the induced fluorescence. The product state distribution of OH $X\ ^2\Pi$ is highly nonstatistical, with a strongly inverted rotational distribution for v″=1, demonstrating that a significant torque is applied to OH as 4.0 eV of purely electronic energy is converted into internal excitation of the OH $X\ ^2\Pi$ (v″, J″) products. The high degree of rotational excitation appears to be a direct manifestation of the forces in the vicinity of the conical intersection region(s) that lead to quenching.[2] Thus, the highly nonstatistical OH $X\ ^2\Pi$ product state distribution observed following quenching of OH $A\ ^2\Sigma^+$ by molecular hydrogen provides valuable new information on the dynamical pathway through the conical intersection region(s) in the HO-H_2 system.

More recently, we reported a combined experimental and theoretical investigation of the inelastic scattering channel resulting from electronic quenching of OH $A\ ^2\Sigma^+$ by molecular hydrogen.[5] The experiments utilize a pump-probe scheme to determine the OH $X\ ^2\Pi$ population

distribution following collisional quenching in a pulsed supersonic expansion. The pump laser excites OH $A\,^2\Sigma^+$ (v'=0, N'=0), which has a significantly reduced fluorescence lifetime due to quenching by H_2. The probe laser monitors the OH $X\,^2\Pi$ (v'', N'') population via laser-induced fluorescence on various A-X transitions under *single-collision* conditions. The experiments reveal a high degree of rotational excitation (N'') of the quenched OH $X\,^2\Pi$ products observed in v''=1 and 2 as well as a pronounced propensity for quenching into the $\Pi(A')$ Λ-doublet level. These experiments have been supplemented by extensive multi-reference, configuration-interaction calculations aimed at exploring the topology of the relevant potential energy surfaces. Electronic quenching of OH $A\,^2\Sigma^+$ by H_2 proceeds through conical intersections between two potentials of A' reflection symmetry (in planar geometry) that correlate with the electronically excited $A\,^2\Sigma^+$ and ground $X\,^2\Pi$ states of OH. The conical intersections occur in high-symmetry geometries, in which the O-side of OH points toward H_2. Corroborating earlier work of Hoffman and Yarkony,[2] these calculations reveal a steep gradient away from the OH–H_2 conical intersection as a function of both the OH orientation and interfragment distance. The former will give rise to a high degree of OH rotational excitation, as observed for the quenched OH $X\,^2\Pi$ products. An additional potential energy surface of A'' reflection symmetry, correlating with OH $X\,^2\Pi$ + H_2, does not have this pronounced angular gradient and, as a result, coplanar passage through the conical intersection would favor the observed $\Pi(A')$ Λ-doublet propensity.

The terminal funding was used to complete the experimental project described above, primarily through support of graduate student Logan Dempsey, and writing up several manuscripts for publication.[5-7]

Equipment

N/A

Personnel

This grant has partially supported the research of graduate students Margaret Greenslade, Erika Derro, Ilana Pollack, Logan Dempsey, and Eunice Li. In addition, postdoctoral researchers Patricia Cleary, Craig Murray, and Ian Konen worked part-time on this project.

Interactions/Transitions

I have collaborated with Millard Alexander on the theoretical aspects of this project and had informal discussions with David Yarkony. I have also worked with Rainer Dressler and colleagues at Hanscom AFB on the analysis of OH emission data from the Space Shuttle's thruster plume.

Inventions and patent disclosures

There have been no inventions leading to patent disclosures during the period of this grant.

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